

Relaxation of C₆₀ in solutions and films: results of femtosecond measurements

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Femtosecond laser spectroscopy has revealed a substantial difference between the relaxation properties of C₆₀ in solutions and in films at excitation intensities 10¹⁰–10¹¹ W/cm². An absorption increase with a time scale of 1.2 ps is observed in the solution. This increase is attributed to a restructuring of the molecule after the absorption of a photon. In the film, the induced absorption undergoes a nonexponential decay, at a rate which increases with increasing excitation intensity. This effect is attributed to singlet-singlet annihilation.

The properties of the fullerenes—closed molecules in which carbon atoms lie on a spherical or spheroidal surface—are attracting a huge amount of research interest. Among the various fullerenes, the molecule C₆₀, with the highest symmetry, is attracting the most attention. Interest in these properties increased dramatically after the discovery of a superconductivity of C₆₀ when doped with alkali metal atoms.¹ The many delocalized electrons in the C₆₀ molecule give this molecule a very nonlinear behavior in an optical field. There is thus the possibility of utilizing these molecules to limit the intensity of laser light to protect optical sensors and also to create nonlinear elements for optical digital processors.² Yet another unique property of C₆₀ is the stability of isolated molecules with respect to fragmentation upon the absorption of a large number of photons and the related effect of retarded ionization.³

There is accordingly interest in the behavior of C₆₀ molecules, both isolated molecules and in a condensed phase, which have absorbed one or several photons. Despite the long list of publications on C₆₀, only a few have reported experiments on relaxation properties of this molecule. So far, the research on the relaxation of the molecule in solutions, with time resolutions as high as 1 ps, has failed to reveal processes which are faster than intercombinational conversion from the S₁ excited state, whose time scale has been reported variously from 33 ps (Ref. 4) to 1.2 ns.^{5,6} The only exceptional case is the study by Talapatra *et al.*,⁷ who used a method involving a Kerr optical shutter, after excitation of the molecule by a 60-fs laser pulse. They observed a relaxation of the nonlinearity over a time shorter than the pulse length. It appears extremely likely to us that the observed response was due not to C₆₀ molecules but to nonlinear effects in the solvent and in the material of the cell holding the sample (more on this below). Contradictory data have been reported by

different investigators on the stability of C_{60} molecules in solution with respect to illumination.

In experiments with C_{60} films, a fast nonexponential response has been observed in several places⁸⁻¹⁰ after excitation of the sample by an ultrashort laser pulse. A 300-fs pulse at the wavelength 605 nm, with an intensity up to 2×10^8 W/cm², was used in Ref. 8 for excitation. The films were probed at the same wavelength. The observed relaxation of the induced absorption was described well by a function $\exp[-(t/\tau)^\beta]$ with $\beta=0.43$ and $\tau=43$ ps. This relaxation was linked with a hopping mechanism for carrier relaxation, including a tunneling of electrons between localized states. Rosker *et al.*⁹ carried out some experiments on degenerate four-wave mixing, using for excitation a 150-fs pulse at 633 nm with an intensity up to 10^9 W/cm². The relaxation observed in that experiment was described by three exponential functions with time scales of 10^{-13} , 10^{-12} , and 10^{-10} s. The nature of the fast components was not resolved. Thomas *et al.*¹⁰ studied the relaxation of excited carriers in a C_{60} film by absorption spectroscopy. The intensity of the excitation by the 100-fs pulse at 600 nm ranged up to 10^{12} W/cm². The induced absorption was probed in the spectral interval 1.5–2.6 eV by means of a femtosecond-range continuum pulse. Thomas *et al.* observed two relaxation times: 2 ps, which was linked with an intramolecular electron-phonon relaxation, and 1.7 ns, which reflected the lifetime of an excited singlet. It is possible that the contradictory conclusions reached by the various investigators regarding the relaxation mechanism result from the different excitation intensities used in the different experiments.

In this letter we are reporting a study of the kinetics of the absorption in C_{60} solutions and films by absorption spectroscopy with a time resolution of 10^{-13} s. The measurements were taken after excitation by a 230-fs pulse at 592 nm. The excitation intensity was varied over the range 10^{10} – 10^{11} W/cm² with the help of neutral filters. The spectral region of the probing by a continuum pulse was 400–900 nm. The delay of the probe pulse was varied from 200 ps to 2 ps at steps of 10 fs. Each point of the kinetics was found by averaging 2000 laser pulses. The error in the determination of the optical density in the difference spectrum was $(2-3) \times 10^{-4}$. The test samples were toluene solutions of C_{60} with an optical density of 0.2. The solution was held in a rotating glass cell 1.4 mm thick. We also studied a C_{60} film on a quartz substrate, with an optical density of 0.45 (these optical densities refer to the excitation wavelength). The line spectra of the samples turned out to be similar to those reported in Refs. 5, 11; these spectra were measured twice a day, before and after the experiment.

1. It was observed that the line spectrum of the solution does not change during the experiment at any excitation intensity studied. The line spectrum of the film also remains constant up to 2×10^{10} W/cm². In addition, the kinetics of the difference spectra reproduces well under these conditions after prolonged illumination of the sample. This result is evidence that no irreversible changes occur in the samples. Irreversible changes do appear in the film (there is a darkening visible to the eye) at an excitation intensity of 5×10^{10} W/cm²; the relaxation properties of the film change noticeably in the process.

2. In measurements of the kinetics of solutions in the spectral interval 500–700

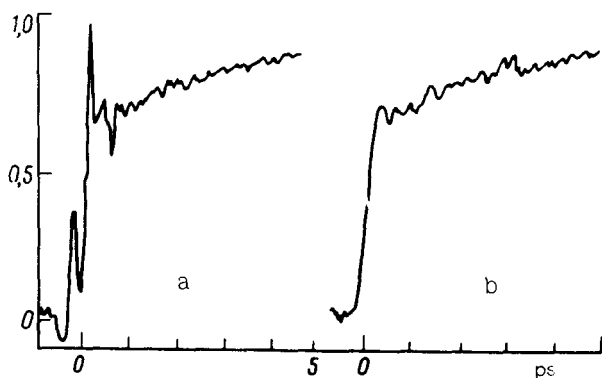


FIG. 1. Normalized kinetic curves of the absorption of C_{60} in toluene recorded by probing at (a) 650 and (b) 410 nm.

nm at the “front of the kinetics,” i.e., during the overlap of the exciting and probe pulses, oscillations with a typical period of 100–140 fs are observed in the sample (Fig. 1a). Additional experiments with a pure solvent and with an empty cell showed that the source of these oscillations was not the C_{60} molecules but the solvent and the cell material. We believe that the reason for the observed oscillations is the joint effect of two-photon absorption in the toluene, the onset of a nonlinear increment in the refractive index, and a pulsed stimulated Raman scattering.¹²

3. After an analysis of the kinetics in light of these effects, the kinetics took the same form as that at 410 and 800 nm, where solvent effects were not seen (Fig. 1b). Consequently, a rapid jump in absorption, due to the excitation of C_{60} , was observed in the kinetics over the entire spectral region; the speed of this jump was determined by the pulse length. After this jump, the absorption increased further because of a disruption of the symmetry of the molecule as its structure changed (the Jahn–Teller effect), with a time scale of 1.2 ps. At the accuracy of our measurements, this time was independent of the excitation intensity. We did not observe any longer relaxation times in the range of delay times used (up to 50 ps). This result agrees with the data of Refs. 5 and 6 on the interconversion time, 1.2 ns.

4. Figure 2 shows the difference absorption spectrum of C_{60} and toluene for a probe delay of 4 ps, as found from the kinetic data at various wavelengths. The shape of the spectrum agrees well with data on the excited state S_1 of C_{60} .^{5,6} Comparison of the spectrum in Fig. 2 with the spectra of triplet-triplet absorption¹³ shows that C_{60} in the S_1 state, like that in the T_1 triplet state, has a wide absorption band. The absorption from S_1 is stronger than that from T_1 in the regions 400–650 and 795–900 nm, indicating there may be an effective optical limitation of pulses in the picosecond and femtosecond ranges.

5. We observed a sharp difference in the nature of the relaxation in the solutions and in the film under identical excitation conditions (compare Figs. 1 and 3). The Jahn–Teller effect was not exhibited in the film. We believe that the reason is a disruption of the symmetry of the molecule in its initial state because of solid-state effects, as can be seen in the line spectra of some films.¹¹ The photoinduced absorption in the film relaxes in a nonexponential way, at a rate which increases with increasing

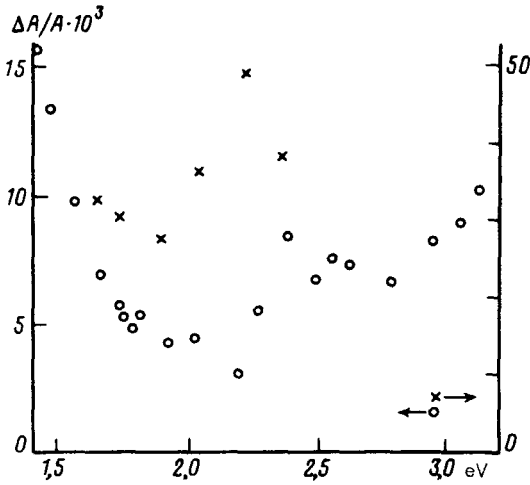


FIG. 2. Difference spectra of (o) a solution and (x) a film of C_{60} .

excitation intensity (Fig. 3). In addition, we see a spectral dependence of the relaxation rate, with a peak at 650 nm. The increase in the relaxation rate with increasing density of excited molecules indicates that this relaxation is of an intermolecular nature. The relaxation mechanism is apparently singlet-singlet exciton annihilation.¹⁴ The formation of highly excited singlet states as a result of this process may lead to irreversible photochemical changes in the sample, such as polymerization.¹⁵

6. Figure 2 shows the difference spectrum of a C_{60} film near a zero delay (near the maximum signal). This spectrum has a peak near 2.25 eV, in agreement with the results of Ref. 10, but the spectrum in Fig. 2 does not have the sharp decay observed in Ref. 10 at lower energies. The reason may be either the higher excitation intensity used in Ref. 10 (at such intensities in our own experiments, we observed an irreversible change in the sample, apparently due to a polymerization of C_{60} molecules,¹⁵ which leads to changes in the relaxation characteristics of the material) or an inadequate intensity of the probe continuum in this spectral region in Ref. 10.

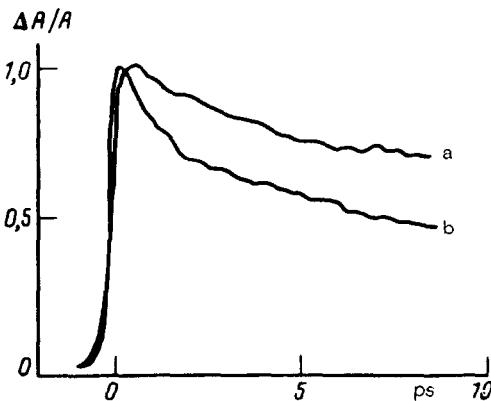


FIG. 3. Normalized kinetic curves of the absorption of a C_{60} film at 650 nm. (a) Excitation intensity of 10^{10} ; (b) 2×10^{10} W/cm².

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